SESSION XVII

P^2 INITIATIVES

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Development of Environmentally-Compliant Surface Treatments

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Abstract

Stricter environmental regulations have banned the use of chromate-based treatments as a part of corrosion inhibition packages for aluminum-skinned aircraft. This, combined with the push for increased aircraft lifetimes, has lead to the need for development of environmentally-compliant coatings. The sol-gel method is being investigated as an environmentally-compliant alternative for chromate-based conversion coatings. Thin films prepared via the sol-gel method are water-based with low VOC emissions, dense, and chemically inert. Results of corrosion resistance tests will be discussed.

Introduction

Recently, stricter environmental regulations have mandated that chromate-based treatments be removed from corrosion inhibition packages for aluminum-skinned aircraft. Replacement coating systems must be capable of satisfying the need for dramatically extended aircraft lifetimes, must be compatible with present and future environmental requirements, and must be easily integrated into the current primer/topcoat paint systems.

Since the preparation of the first silicon alkoxide in 1846, the sol-gel method has emerged as a versatile method for preparing a host of oxide materials[1]. The sol-gel method consists of simultaneous hydrolysis and condensation reactions originating with alkoxide precursors to form a polymeric network of micro- or nanoporous glass as shown in equations 1 and 2.

(1) Hydrolysis $Si(OR)_4 + 4H_2O \rightarrow Si(OH)_4 + 4ROH$
(2) Condensation $Si(OH)_4 + Si(OH)_4 \rightarrow (OH)_3Si\text{-}O\text{-}Si(OH)_3 + H_2O$

Prior to gelation, the sol is ideal for preparing thin films by common processes, including dipping, spinning, or spraying[1,2]. Sol-gel materials are candidates for use in passivating film applications, as it is possible to form glassy, highly adherent, chemically inert films on metal substrates at room temperature.

Ormosils are hybrid organic-inorganic materials composed of intimately mixed polymer systems. Ormosil films are of interest because they blend the mechanical and chemical characteristics of the comprising networks. The inorganic regions impart durability, scratch resistance, and improved adhesion to the aluminum alloy substrates, while the organic regions impart increased flexibility, density, and functional compatibility with organic polymer paint systems. Hybrid films may be tailored to have exceptional durability and adhesion, while providing a dense, flexible barrier to permeation of water and corrosion initiators.

In the present study, sol-gel derived thin films have been investigated for use as environmentally-compliant alternatives to chromate-based conversion coatings. The results of this study indicate that sol-gel derived coatings are promising candidates for environmentally-compliant alternatives for the chromate-based conversion coatings in use today.

Experimental

Materials and Reagents: Substrates consisted of aluminum 2024-T3 coupons which were polished with 400 and 600 grit silicon carbide sand paper followed by cleaning in an ultrasonic bath using isopropanol and hexane solvents. Tetraethoxysilane (TEOS) and 3-glycidoxypropyltrimethoxysilane (GPTMS) were used as received from Aldrich. Surfactants were incorporated by direct dissolution into the aqueous sol. Nitric acid was used to catalyze the hydrolysis reaction.

Sol-Gel Thin Film Preparations: Preparation of ormosil solutions may be summarized as follows: 11.1 ml of TEOS were placed in a beaker with 3.6 ml of acidified water. The resultant two-phase solution was vigorously stirred to induce mixing and initiate hydrolysis. The sol was stirred for approximately 1 hour, followed by addition of GPTMS to the clear, single phase solution. Surfactants were added in a drop-wise manner until the desired concentrations were obtained.

Coating and Curing Methods: Aluminum 2024-T3 substrates were dipped into precursor sols using single dip step using a dwell time of 10 seconds in the coating sol. The withdrawal speed was 10 cm/s into room temperature air. After dipping, the samples were cured overnight in a 60 °C oven, followed by 24 hours in a 120 °C oven. After heat treatment, the samples were allowed to cool to room temperature.

Paint Systems: [Urethane primer/urethane topcoat], [epoxy primer/urethane topcoat], and self priming topcoat were used as primer/topcoat systems in this study.

Corrosion Resistance Tests: Ormosil-coated test coupons were placed in a 5% salt spray solution for 1000 hours. After removal from the salt fog chamber, the samples were rinsed with distilled water to remove any residues.

Results

Corrosion Resistance Tests

Protective properties of hybrid sol-gel films were determined in relation to 2024-T3 aluminum coupons which were (a) untreated and pretreated with (b)phosphoric acid, (c) alodine, and (d) phosphoric acid and alodine. Film performance was studied as a function of surface treatments.

Epoxy Primer/ Urethane Topcoat System

Figure 1 shows the results of the 1000 hour salt spray corrosion resistance test for aluminum samples treated as follows: (a) bare aluminum, (b) phosphoric acid pretreatment, (c) alodine pretreatment, (d) phosphoric acid wash followed by alodine pretreatment, and (e) sol-gel coating. Moderate corrosion in the scribe mark and blistering which extends 1/16 to 1/8" from the center of the scribe mark is observed on the bare aluminum panel (Figure 1a). While decreasing the extent of blistering observed, phosphoric acid or alodine pretreatment resulted in increased concentrations of corrosion within the scribe mark, indicating degradation in the corrosion resistance performance of the primer/ topcoat system (Figures 1b and 1c). Pretreatment with both phosphoric acid and alodine decreases the amount of blistering observed (Figure 1d). Treatment with the sol-gel coating lead to a significant improvement in the corrosion resistance behavior of the samples tested, as only light to moderate corrosion in the scribe marks and no blistering was observed (Figure 1e).

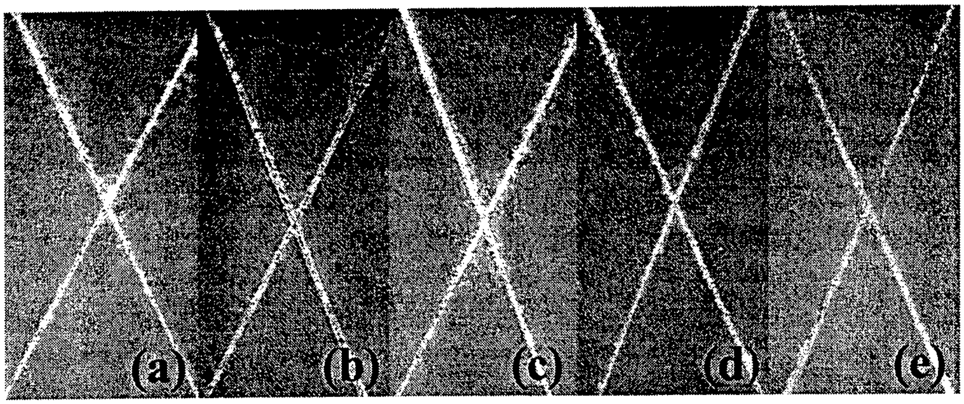

Figure 1: Results of corrosion resistance test for aluminum coupons which have been treated, prior to application of epoxy primer/ urethane topcoat system, as follows: (a) untreated, (b) phosphoric acid pretreatment, (c) alodine pretreatment, (d) phosphoric acid and alodine pretreatments, and (e) sol-gel coating.

Urethane Primer/ Urethane Topcoat System

Figure 2 shows the results of 1000 hour salt spray corrosion resistance tests for the urethane primer/ urethane topcoat system. In the untreated sample, extremely heavy corrosion and blistering are observed (Figure 2a). Addition of phosphoric acid decreases the amount of corrosion in the scribe mark, but dramatically increases the amount of blistering observed (Figure 2b). Alodine pretreatment, significantly reduces the extent of corrosion and no blistering is observed (Figure 2c). The moderate corrosion and blistering observed in Figure 2d indicate that dual pretreatments with phosphoric acid and alodine improve the corrosion resistance characteristics compared to bare aluminum. However, when used in conjunction with the urethane primer/urethane topcoat system, phosphoric acid pretreatment appears to degrade the performance of the alodine pretreatment. The appearance of the coupon treated with the sol-gel coating is comparable to that of the coupon treated with alodine: light to moderate corrosion is observed in the scribe mark and only slight blistering is observed (Figure 2e).

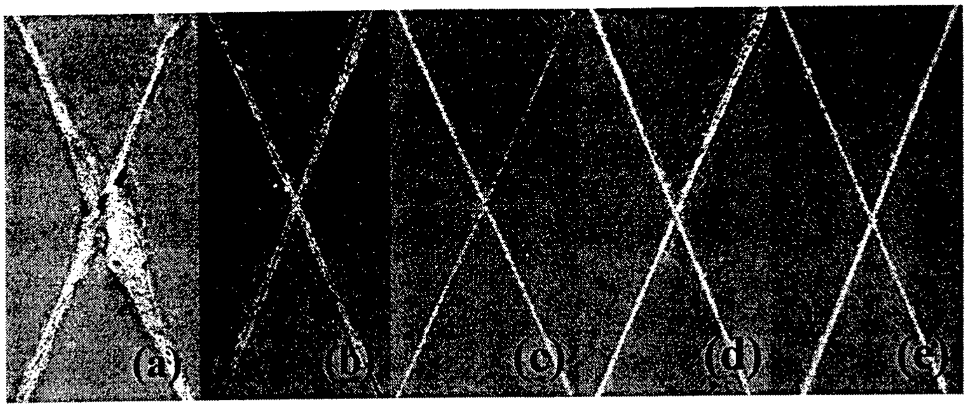

Figure 2: Results of corrosion resistance test for aluminum coupons which have been treated, prior to application of urethane primer/ urethane topcoat system, as follows: (a) untreated, (b) phosphoric acid pretreatment, (c) alodine pretreatment, (d) phosphoric acid and alodine pretreatments, and (e) sol-gel coating.

<u>Self-Priming Topcoat System</u>

Compared to the epoxy and urethane primer/topcoat systems, the self-priming topcoat system appears to provide minimal corrosion resistance as indicated by the extremely heavy corrosion and paint peeling observed in Figure 3a. Pretreatment with either phosphoric acid or alodine appear to improve the corrosion resistance slightly, though heavy corrosion and blistering/peeling is observed on the bare aluminum surface (Figure 3b and 3c). Combination of phosphoric acid and alodine pretreatment improves the passivation effect, as indicated by a reduction in the concentration of corrosion and blistering (Figure 3d). Use of the sol-gel coating (Figure 3e) shows dramatic improvements in the corrosion resistance behavior of the coupons tested, as blistering is not observed and corrosion is moderate and within the scribe mark.

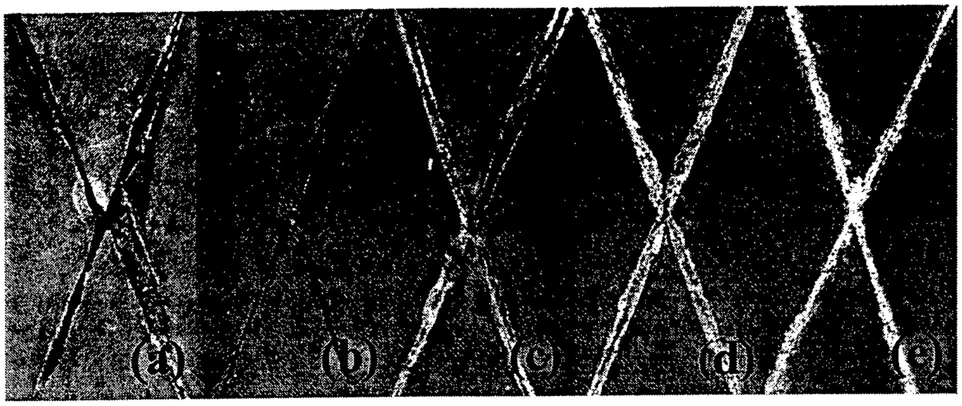

Figure 3: Results of corrosion resistance test for aluminum coupons which have been treated, prior to application of self-priming topcoat system, as follows: (a) untreated, (b) phosphoric acid pretreatment, (c) alodine pretreatment, (d) phosphoric acid and alodine pretreatments, and (e) sol-gel coating.

Discussion

Chemical conversion coatings are used to enhance the corrosion resistance of a surface through forming a barrier which inhibits the penetration of corrosion initiating species and increasing the paint adhesion[3]. In this study, the effectiveness of sol-gel coatings was compared to the effectiveness of three primer topcoat systems and three surface pretreatment procedures which are currently in use for the passivation of aluminum skinned aircraft. Prior to any surface pretreatment, the epoxy, urethane, and self-priming topcoat systems showed minimal corrosion resistance capabilites. In all three systems, use of the chromate-based alodine pretreatment lead to improvements in the corrosion resistance abilities of the primer/topcoat system. Phosphoric acid pretreatment increased the tendency for blistering/peeling. Combination of phosphoric acid and alodine pretreatments generally improved the corrosion resistance behavior of the paint systems by confining corrosion to the scribe marks and minimizing the amount of blistering which was observed. In all three primer/ topcoat systems, use of a sol-gel coating led to significant increases in the corrosion resistance behavior of the paint system.

Thin films prepared using the sol-gel method are characteristically chemically inert and impenetrable by water and other corrosion initiating ions. Because the degree of secondary barrier action depends on the continuity, compactness, and stability of the corrosion product layer[3], variation in the chemical composition of the ormosil sol leads to variation in the properties of the resulting thin film. Sol-gel derived thin films are promising, environmentally-compliant alternatives to chromate-based conversion coatings presently used for passivation of aircraft aluminum alloys.

References

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